THE ROLE OF SONICATION OF POLYETHYLENEOXIDE SOLUTIONS CONTAINING MAGNETIC NANOPARTICLES ON MORPHOLOGY OF NANOFIBROUS MATS

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Abstract

Properties of the resulting polymer nanofibers are often tailored by sonication technique applied prior or past an electrospinning process. The aim of this contribution is to evaluate morphology of nanofibrous mats formed by poly(ethylene oxide) with distributed magnetic nanoparticles (MNP) (about 20 nm in diameter) in dependence on time of sonication of the used polymer solutions. The solutions were exposed to sonication (intensity 200W, frequency 24 kHz) for 10, 30, and 60 minutes. It was shown that rheological characteristics (viscosity, storage and loss moduli) strongly depend on time of sonication (particularly phase angle) in contrast to electric conductivity and surface tension. For analysis of homogeneous distribution of MNP in polymer solution, the rheological measurements were carried out also in presence of external magnetic field. Magnetorheological efficiency (a relation of corresponding viscosities) was determined for 80, 170, and 255 mT. Consequently, changed rheological characteristics participate significantly in the process of electrospinning and resulting quality of the obtained nanofibrous mats. Qualitative changes were described by means of scanning electron microscopy (variance of mean diameter of nanofibers), transmission electron microscopy (distribution of MNP within nanofibrous mats). Static magnetic properties were determined by a vibration sample magnetometer. It was shown that even distribution of MNP in the mats can be achieved by mere sonication process without application of external magnetic field during an electrospinning process. However, time of sonication generates a degree of embedding of MNP into individual nanofibers.

Keywords: Ultrasound, poly(ethylene oxide), magnetic nanoparticles, magnetorheology, electrospinning

1. INTRODUCTION

Electrospinning is based on evoking viscoelastic usually polymer jets in intensive electric field (~kV/cm). After passing a distance between a source of polymer solution and a collector, used solvent should be optimally completely evaporated and an obtained nanofibrous mat should consist of a pure polymer material. This ranges an electrospinning process to a relatively simple but very efficient method producing nanofibers.

Nevertheless, this process subjects too many input parameters [1, 2] basically divided into four categories characterizing: 1) polymer material (molecular weight, molecular weight distribution, topology of macromolecules), 2) solvent (surface tension, solubility parameters, relative permittivity), 3) solution (viscosity, concentration, specific conductivity), and 4) basic process parameters (electric field strength, tip-to-collector distance, temperature, humidity).

In addition to basic process parameters, there exists a series of possibilities how to influence quality and practical application of the final electrospun products. In this respect sonication process as a non-invasive method has recently attracted attention both in pre-electrospinning stage as well as in the post-electrospinning phase. This process makes the electrospun mats possible to apply in various branches as for instance biomedicine (magnetic targeted therapy, magnetic cell separation or magnetic treatment of tumors [3]) for which some attributes can be successfully tailored.

Basically, there are three approaches in preparing polymer solutions for electrospinning: vibrational shaking, magnetic stirring, and sonication. The last approach is effective especially when magnetic nanoparticles (MNP) (usually 2-30 nm in diameter) are inserted into polymer solution [4, 5]. Tarasova [5] compared three different methods of preparation of polymer solution containing conductive filler and showed a strong influence of an employed method on final morphology of the fibers, their conductive and mechanical properties. As expected, polymeric material during sonication process exhibits non-negligible degradation [6].

The aim of this contribution is to relate morphological changes of poly(ethylene oxide) (PEO) electrospun nanofibrous mats containing MNP to magnetorheological characteristics of source material for homogenization of which sonication process is applied. Distribution (homogeneity) of MNP in the resulting mats was evaluated using a scanning electron microscope, a transmission electron microscope, and a vibrating sample magnetometer.

2. EXPERIMENTAL PART

PEO (Sigma Aldrich, USA, molecular weight 300,000 g/mol) was dissolved in distilled water (9 wt.%) and magnetically stirred at 250 rpm under 25 °C for 48 hrs. MNP were prepared under microwave assisted radiation ensuring homogeneous conditions during the synthesis [7]. All chemicals used were in reagent grade (Penta, Czech Republic). The diameter of the prepared MNPs was around 20 nm.

Prepared MNPs were dispersed (5 wt.%) in aqueous PEO solution. To improve their dispersion, an ultrasonic processor UP200S (Hielscher, Germany) equipped with a sonotrode (2 mm in diameter) providing sonication intensity of 200 W and frequency 24 kHz was applied for 0, 10, 30, and 60 minutes.

A rotational rheometer Physica MCR 501 (Anton Paar, Austria) was used in two geometrical arrangements. The first one with no external field was represented by concentric cylinders (diameter 27 mm) and the second one by the magnetorheological cell Anton Paar 180/1T in configuration of parallel plates (diameter 20 mm) where consecutively three values of strength of magnetic intensity were set: 80, 170, and 255 mT.

The electrospinning process (more details in [8]) was carried out at voltage of 25 kV with the tip-to-collector distance fixed to 200 mm under ambient conditions (temperature 21±1 °C and relative humidity 64±1 %).

Morphology of resulting nanofibrous mats was analyzed using a Vega 3 high resolution scanning electron microscope (Tescan, Czech Republic). For a determination of mean fiber diameter, 300 fibers were taken from 3 different images using Adobe Creative Suite software. Topology of MNPs within the nanofibrous mats and nanofibers themselves was studied using a transmission electron microscope Philips CM 12 (wolfram cathode; operated at 120 kV). The microscope was equipped with a high tilt holder (±45°) that was used for the checking of particle positions (inside/outside fibers). Magnetostatic properties of nanofibrous webs were evaluated by a vibrating sample magnetometer VSM 7407 (Lake Shore, USA) at ambient temperature (25 °C) in a magnetic field up to 10 kOe (~800 kA/m). The amplitude and the frequency of vibration attained 1.5 mm and 82 Hz, respectively.

3. RESULTS AND DISCUSSION

Duration of sonication process during incorporation of MNPs into aqueous PEO solution prior to electrospinning has a significant impact to rheological behavior of the resulting source material. Longer sonication implies chain scission of PEO macromolecules as documented by lowering average molecular weight as well as index of polydispersity (see also [9]). This simultaneously causes a decrease in shear viscosity and a prolongation of Newtonian plateau with time of sonication (**Figure 1**). These two factors are accompanied by deagglomeration of MNPs in a solution.

Simultaneously with a decrease in shear viscosity with time of sonication, there is also a drop in storage modulus. In other words, elasticity is reduced which is reflected in worse morphology of nanofibrous mats - appearance of so called beads.

For analysis of homogeneity of MNPs distribution in polymer solution, the rheological behavior of aqueous PEO solutions with MNPs was also characterized in the presence of an external magnetic field (**Figure 2**).

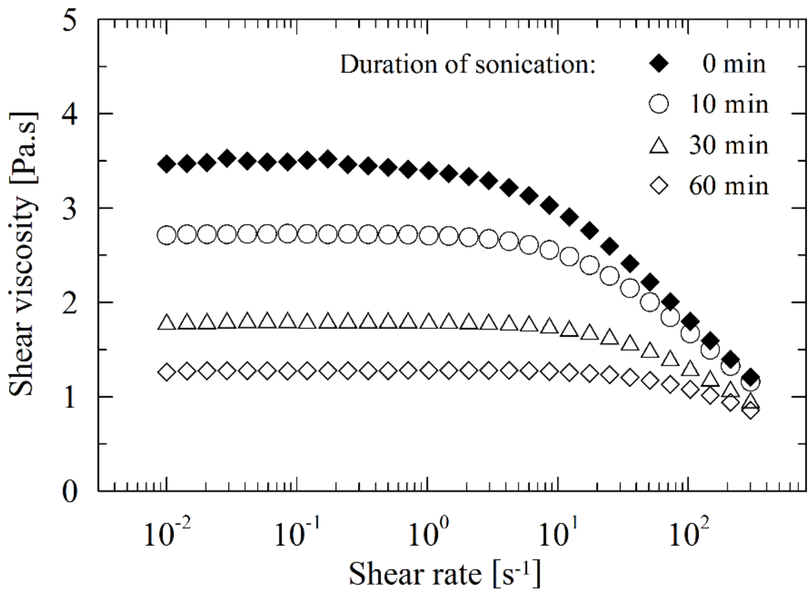

Figure 1 Shear viscosity of aqueous PEO solutions with MNPs in dependence on shear rate

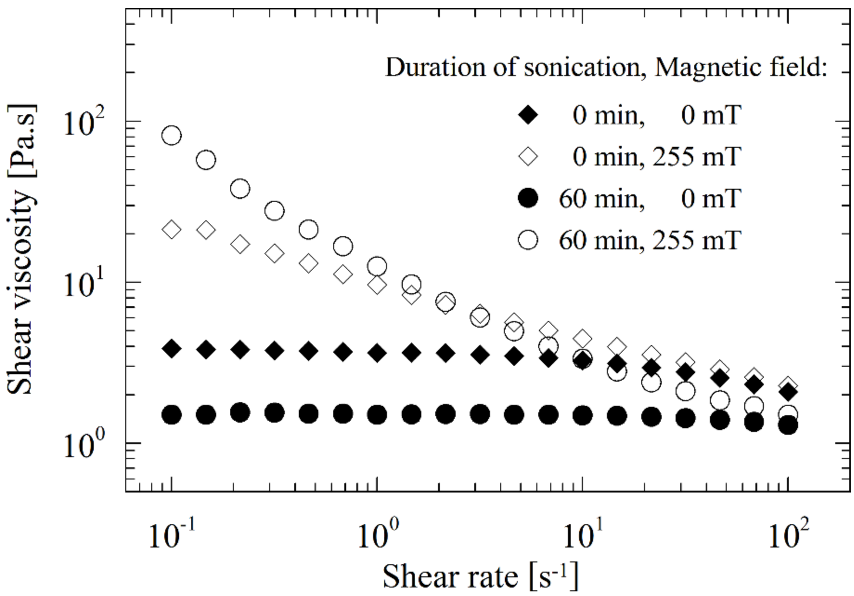

Figure 2 Shear viscosities of aqueous PEO solutions with MNPs in dependence on shear rate in the presence/absence of an external magnetic field

The magnetorheological behavior is significantly influenced by the duration of sonication. While the viscosity of the system decreases in the absence of magnetic field, the opposite tendency occurs when the magnetic field is employed. Due to the lower viscosity of the polymer solution and deagglomeration of MNPs, the magnetized MNPs can more easily move, attract each other due to magnetic dipole-dipole interactions and thus create stiffer and more shear-resistant structures.

The fibers of higher quality (circular in diameter, beadless) were spun from non-sonicated aqueous PEO solution with MNPs. Gradually, as the duration of sonication increased, the quality of fibers deteriorated. The mean fiber diameter dropped by 39 % after 60 min of sonication and the presence of numerous beads varying in the size appeared (**Figure 3**). In addition; as the size of agglomerates decreases with duration of sonication, the MNPs are more homogeneously distributed within the electrospun fibers. These results correlate very well with literature data [9, 10], where the impact of viscosity, elasticity and polydispersity on the quality of fibers was documented.

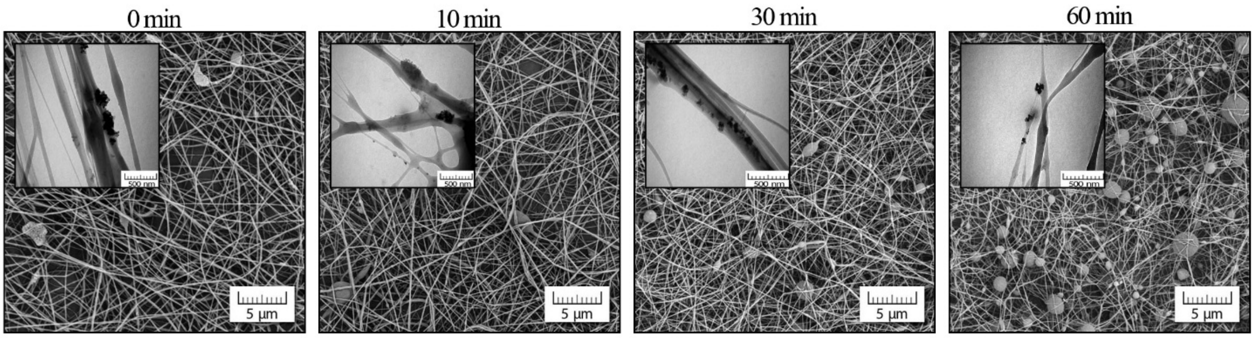

Figure 3 Morphology of nanofibrous mats electrospun from aqueous PEO solutions with MNPs in dependence on time of sonication (SEM (larger) and TEM (smaller insets) pictures)

The type of particle positions (inside/outside fibers) was also checked by observing at various holder tilts in TEM analysis. The overall saturation magnetization of prepared composite structures is much lower (9 $emu \cdot g^{-1} = 9\ A \cdot m^2 \cdot kg^{-1}$) than that of the pure MNPs (76 $emu \cdot g^{-1} = 76\ A \cdot m^2 \cdot kg^{-1}$) [7] due to the contribution of nonmagnetic polymer matrix. It is worth mentioning that the saturation magnetization of nanofibrous mats is virtually unaffected by the sonication time indicating that the amount of magnetic phase is identical in all composites.

4. CONCLUSION

The considerable impact of sonication on the final properties and application of PEO solutions containing MNPs was approved. The sonication contributes to better implementation of MNPs into the structure of electrospun nanofibers as confirmed by scanning and transmission electron microscopy. Due to the chain scission and deagglomeration of MNPs the shear viscosity significantly decreases with respect to its original value. On the other hand, aqueous PEO solutions lose their elasticity which contributes negatively to the quality of electrospun nanofibers.

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